

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In the matter of an application for a German Patent

with the file reference 103 56 099.8

filed on 27 November 2003

in the name of Covion Organic Semiconductors GmbH, Frankfurt, Germany,

and in the matter of an application for a United States Patent.

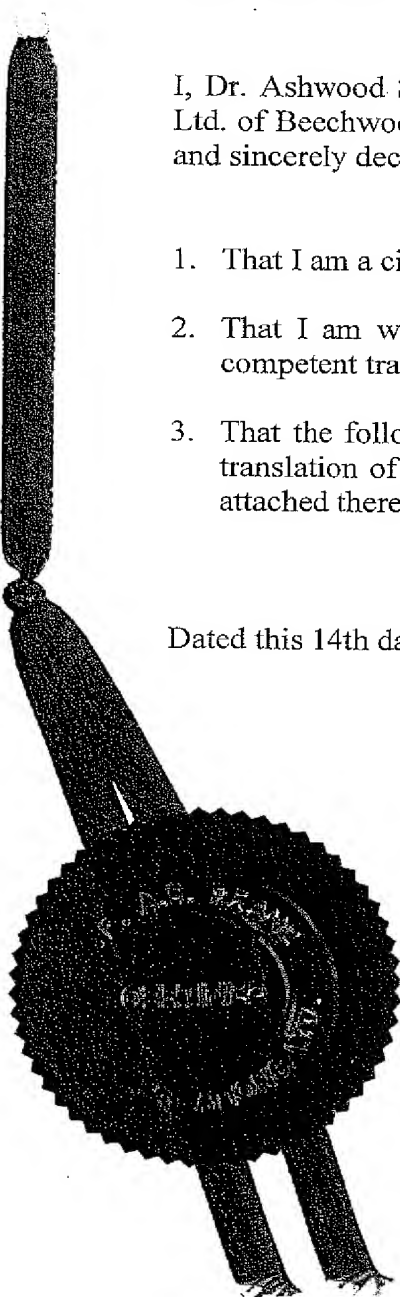
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1. That I am a citizen of the United Kingdom of Great Britain and Northern Ireland.
2. That I am well acquainted with the German and English languages and am a competent translator thereof.
3. That the following is to the best of my knowledge and belief a true and correct translation of the above-referenced patent application and the Official Certificate attached thereto

Dated this 14th day of October 2009



Dr. Ashwood Stephen Drane



FEDERAL REPUBLIC OF GERMANY



Priority certificate regarding the filing of a patent application

File reference: 103 56 099.8

Date of filing: 27 November 2003

Applicant/proprietor: Covion Organic Semiconductors GmbH,
65929 Frankfurt/DE

Title: Organic electroluminescent element

IPC: H 01 L, C 07 D, C 09 K

**The attached pages are a correct and accurate reproduction of the
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Munich, 13 January 2005
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On behalf of
The President

[signature]

Brosig

Description

5 Organic electroluminescent element

10 Organic and organometallic compounds are used as functional materials in a number of applications of different types which can be ascribed to the electronics industry in the broadest sense. The organic electroluminescent devices based on organic components (general description of the structure cf. US-A-4,539,507 and US-A-5,151,629) and the individual components thereof, organic light-emitting diodes (OLEDs), have already been introduced onto the market, as confirmed by the automobile radios with an "organic display" from Pioneer or a digital camera from Kodak. Further products of this type are just about to be introduced. Nevertheless, significant improvements are still necessary here in order to make these displays a true competitor to the liquid-crystal displays (LCDs) which currently dominate the market, or to surpass the latter.

20 A development which has emerged in recent years is the use of organometallic complexes which exhibit phosphorescence instead of fluorescence (M.A. Baldo *et al.*, *Appl. Phys. Lett.* **1999**, 75, 4-6). For theoretical spin-statistical reasons, an up to four-fold energy and power efficiency is possible using organometallic compounds as phosphorescence emitters. Whether this new development will succeed is highly dependent on whether it is possible to find corresponding device compositions which are also able to implement these advantages (triplet emission = phosphorescence compared with singlet emission = fluorescence) in OLEDs. It is not only the development of the organometallic compounds themselves that is of importance here, but also, in particular, the development of further materials specifically required for this purpose, such as, for example, matrix or hole-blocking materials.

30 An organic electroluminescent device usually consists of a plurality of layers applied one on top of the other by means of vacuum methods or various printing techniques. For phosphorescent organic electroluminescent devices, these layers are in detail:

- 35 1. outer plate = substrate (usually glass or plastic sheet);
2. transparent anode (usually indium-tin oxide, ITO);
3. hole-injection layer (HIL): for example based on copper phthalocyanine (CuPc) or conductive polymers;

4. hole-transport layer(s) (HTL): usually based on triarylamine derivatives, for example 4,4',4''-tris(N-1-naphthyl-N-phenylamino)triphenylamine (NaphDATA) as the first layer and N,N'-di-(1-naphthyl)-N,N'-diphenylbenzidine (NPB) as the second layer;
5. emission layer(s) (EML): usually comprising a matrix material in phosphorescent devices, for example 4,4'-bis(carbazol-9-yl)biphenyl (CBP) which is doped with a phosphorescent dye, for example tris(phenylpyridyl)iridium ($\text{Ir}(\text{PPy})_3$) or tris(2-benzothiophenylpyridyl)iridium ($\text{Ir}(\text{BTP})_3$);
6. hole-blocking layer (HBL): usually comprising BCP (2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline = bathocuproin) or bis(2-methyl-8-hydroxyquinolato)(4-phenylphenolato)aluminium(III) (BAIq);
7. electron-transport layer (ETL): usually based on aluminium tris-8-hydroxyquinolate (AlQ_3);
8. electron-injection layer (EIL, also known as insulator layer = ISL): thin layer of a material having a high dielectric constant, such as, for example, LiF , Li_2O , BaF_2 , MgO , NaF ;
9. cathode: generally metals, metal combinations or metal alloys having a low work function, thus, for example, Ca , Ba , Cs , Mg , Al , In , Mg/Ag .

Depending on the device structure, a plurality of these layers may also coincide or each of these layers does not necessarily have to be present.

However, there are still considerable problems requiring urgent improvement in order to facilitate high-quality full-colour applications:

1. For example, the operating lifetime of OLEDs, in particular, is still too short, meaning that it has hitherto only been possible to implement simple applications commercially.
2. The short lifetime gives rise to a secondary problem: especially for full-colour applications ("full-colour displays"), it is particularly poor if the individual colours age at different rates, as is currently the case. This results in a significant shift in the white point occurring even before the end of the lifetime (which is generally defined by a drop to 50% of the initial brightness), i.e. the colour fidelity of the representation in the display worsens. In order to circumvent this, some display manufacturers define the lifetime as 70% or 90% lifetime (i.e. drop of the initial brightness to 70% or 90% of the initial value). However, this results in the lifetime becoming even shorter.
3. The ageing processes are generally accompanied by an increase in the voltage. This effect makes voltage-driven organic electroluminescent devices difficult or impossible. However, current-driven addressing is more complex and expensive precisely in this case.

4. Precisely in the case of efficient phosphorescent OLEDs, the requisite operating voltage is quite and therefore has to be reduced in order to improve the power efficiency.
5. Although the efficiency, in particular the power efficiency (measured in lm/W), of phosphorescent OLEDs is acceptable, improvements are still also desired here.
6. The structure of the OLEDs is complex and technologically complicated due to the large number of organic layers; a reduction in the number of layers is desirable for production in order to reduce the number of production steps, thus simplifying the technology and increasing production reliability.

The above-mentioned reasons make improvements necessary in the production of OLEDs.

In the case of phosphorescent OLEDs, a hole-blocking layer (HBL) is usually used after the emitter layer in order to increase the efficiency and lifetime. These device structures are usually optimised according to the criterion of maximum efficiency. BCP (bathocuproin) is frequently used as hole-blocking material (HBM), enabling very good efficiencies to be achieved (for example D.F. O'Brien *et al.*, *Appl. Phys. Lett.* **1999**, 74, 442), but with the crucial disadvantage that the lifetime of the OLEDs comprising BCP is greatly restricted. T. Tsutsui *et al.* (*Japanese J. Appl. Phys.* **1999**, 38, L1502) indicate the low stability of BCP as the reason for the poor lifetime, meaning that these devices cannot be used in high-quality displays. A further hole-blocking material is bis(2-methyl-8-hydroxyquinolato)(4-phenylphenolato)aluminium(III) (BALq). This has enabled the stability and lifetime of the devices to be significantly improved, but with the side effect that the quantum efficiency of the devices comprising BALq is significantly (about 40%) lower than with BCP (T. Watanabe *et al.*, *Proc. SPIE* **2001**, 4105, 175). Kwong *et al.* (*Appl. Phys. Lett.* **2002**, 81, 162) thus achieved lifetimes of 10,000 h at 100 cd/m² using tris(phenylpyridyl)iridium(III). However, this device exhibited an efficiency of only 19 cd/A, which is well behind the state of the art. Thus, although good lifetimes are possible using BALq, overall it is, however, not a satisfactory hole-blocking material since the efficiency achieved is too low.

It is clearly evident from this description that the hole-blocking materials (HBMs) used to date, such as, for example, BCP or BALq, result in unsatisfactory side effects. Thus, there continues to be a demand for hole-blocking materials which result in good efficiencies in OLEDs, but at the same time also result in long lifetimes. Surprisingly, it has now been found that OLEDs which comprise certain

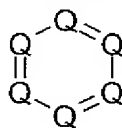
heterocycles – listed below – in particular diazines and triazines, as hole-blocking materials have significant improvements over the prior art. Using these hole-blocking materials, it is possible simultaneously to obtain high efficiencies and good lifetimes, which is not possible using materials in accordance with prior art. In addition, it has been found that an electron-transport layer does not necessarily have to be used with the novel hole-blocking materials, which represents a technological advantage, and that in addition the operating voltages can consequently be significantly reduced, which corresponds to higher power efficiency.

The use of triazines, pyrimidines, pyrazines and pyridazines as emission or charge-transport material in organic electroluminescent devices has already been described in the literature. These materials have been described as fluorescent emitters or in combination with fluorescent emitters. US 6352791 (Bosch) and US 6225467 (Xerox) describe triazines, in particular specifically substituted triazines, as electron-transport materials in OLEDs. A. Bacher *et al.* (*Inorg. and Org. Electroluminescence (Int. Workshop on Electroluminescence)* **1996**, 109-112) report a three-fold higher efficiency if triazine derivatives are incorporated as electron-transport layer between AlQ₃ as emitter and the cathode. No mention is made of the lifetime. Pyrazines as electron-transport materials are described, for example, by T. Oyamada *et al.* (*Chem. Lett.* **2003**, 32, 388). On the other hand, substituted pyrimidine and triazine derivatives can also be employed as hole-transport materials in OLEDs (US 5716722). JP 2002212170 describes triazine derivatives as electrofluorescent compounds, as do J. Pang *et al.* (*J. Mater. Chem.* **2002**, 12, 206).

It is not evident from this prior art how diazine and triazine derivatives could usefully be used in phosphorescent OLEDs since these materials are described both as electron conductors and also as hole conductors or as (fluorescent) emitters. In particular, it is described in the literature by leading experts in the field of phosphorescent OLEDs (R. C. Kwong, M. E. Thompson, S. R. Forrest *et al.*, *Appl. Phys. Lett.* **2002**, 81, 162) that electron-deficient heterocycles, such as, for example, triazines, as hole-blocking materials in phosphorescent OLEDs result in very poor lifetimes, typically in the region of less than 100 h at brightnesses of 500 cd/m², which is well behind the state of the art. A person skilled in the art would have been able to derive from this that this combination is thus unsuitable for achieving a technical improvement. This in no way suggests that good results can be achieved therewith.

The invention relates to an organic electroluminescent device comprising an anode, a cathode and an emission layer, consisting of at least one matrix material which is

doped with at least one phosphorescent emitter, characterised in that a hole-blocking layer which comprises a compound of the formula (1)



(formula 1)

where the following applies to the symbols and indices used:

- Q is on each occurrence, identically or differently, N or CR, with the proviso that at least two and a maximum of four Q stand for nitrogen;
- R is on each occurrence, identically or differently, H, NO₂, CN, N(R¹)₂, a straight-chain; branched or cyclic alkyl or alkoxy group having 1 to 40 C atoms, in which one or more non-adjacent CH₂ groups may be replaced by -R¹C=CR¹-, -C≡C-, Si(R¹)₂, Ge(R¹)₂, Sn(R¹)₂, -O-, -S- or -NR¹- and in which one or more H atoms may be replaced by F, -NR¹- or an aromatic group R¹, or an aromatic or heteroaromatic system or an aryloxy or heteroaryloxy group, each having 1 to 40 aromatic C atoms, in which one or more H atoms may be replaced by F, Cl, Br or I or which may be substituted by one or more non-aromatic radicals R, where a plurality of substituents R may form a further mono- or polycyclic, aliphatic or aromatic ring system, or an aromatic or heteroaromatic system bonded via a divalent group -Z- or an aryloxy or heteroaryloxy group, each having 1 to 40 aromatic C atoms, in which one or more H atoms may be replaced by F, Cl, Br or I or which may be substituted by one or more non-aromatic radicals R, where a plurality of substituents R may form a further mono- or polycyclic, aliphatic or aromatic ring system, or;
- R¹ is on each occurrence, identically or differently, H or an aliphatic, aromatic or heteroaromatic hydrocarbon radical having 1 to 20 C atoms, in which a plurality of substituents R¹ or R¹ with R may also form a further mono- or polycyclic, aliphatic or aromatic ring system, and
- Z is a straight-chain, branched or cyclic, preferably conjugated radical having 1 to 40 C atoms, which is preferably in conjugation with the two other substituents, where the number of atoms in Z which link the group of the formula (1) and the aromatic radical is preferably an even number, where one or more non-adjacent C atoms may be replaced by -O-, -S- or -NR¹- or one or more C atoms may be substituted by a radical R¹ or halogen,
- is incorporated between the emission layer and the cathode.

For the purposes of this invention, an aromatic or heteroaromatic system is intended to be taken to mean a system which does not necessarily comprise only aromatic or

heteroaromatic groups, but instead in which a plurality of aromatic or heteroaromatic groups may also be interrupted by a short non-aromatic unit, such as, for example, sp^3 -hybridised C, O, N, etc. Thus, for example, systems such as 9,9'-spirobifluorene, 9,9-diarylfuorene, triarylamine, etc., should also be understood as aromatic systems.

The OLED may also comprise further layers, such as, for example, hole-injection layer, hole-transport layer, electron-injection layer and/or electron-transport layer. However, it should be pointed out that all these layers do not necessarily have to be present. Thus, it has been found that OLEDs according to the invention which comprise a hole-blocking layer of the formula (1) continue to give comparably good efficiencies and lifetimes with reduced operating voltage if electron-injection and electron-transport layers are not used.

The hole-blocking layer according to the invention preferably comprises at least 50% of compounds of the formula (1), particularly preferably at least 80%, very particularly preferably consists only of compounds of the formula (1).

Preferred structures of the formula (1) contain two or three nitrogen atoms in the ring. These are diazines or triazines, i.e. pyridazines (1,2-diazines), pyrimidines (1,3-diazines), pyrazines (1,4-diazines), 1,2,3-, 1,2,4- or 1,3,5-triazines. Particular preference is given to pyrimidines or triazines, in particular 1,2,4- and 1,3,5-triazines.

Although evident from the description, it should be expressly pointed out here that the hole-blocking material may also comprise more than one such diazine or triazine unit.

Compounds which have proven to be particularly suitable hole-blocking materials are those which have a non-planar structure. While the skeleton (i.e. the six-membered ring of the diazine or triazine) always has a planar structure, corresponding substituents (present in R) may cause a deviation from planarity of the structure as a whole. This is the case, in particular, if at least one of the substituents R contains an sp^3 -hybridised carbon atom (or correspondingly also silicon, germanium, nitrogen, etc.), which consequently has approximately tetrahedral (or in the case of nitrogen pyramidal) geometry.

Preferred hole-blocking materials are therefore compounds of the formula (1) in which at least one substituent R contains at least one sp^3 -hybridised carbon atom. In order to achieve a more significant deviation from planarity, it is preferred for this sp^3 -hybridised carbon atom to be a secondary, tertiary or quaternary carbon atom, particularly preferably a tertiary or quaternary carbon atom, very particularly prefer-

ably a quaternary carbon atom. A secondary, tertiary or quaternary carbon atom is taken to mean a carbon atom having two, three or four substituents other than hydrogen.

Particular preference is given to compounds of the formula (1) which contain a 9,9'-spirobifluorene derivative, a 9,9-disubstituted fluorene derivative, a 6,6- and/or 12,12-di- or tetrasubstituted indenofluorene derivative, a triptycene derivative (preferably linked via position 9 and/or 10) or a tetraarylmethane derivative in at least one of the radicals R. The diazine or triazine or tetrazine unit here may also be bonded, for example, in the 9-position of the fluorene or in the 6- and/or 12-position of the indenofluorene.

Very particular preference is given to compounds of the formula (1) which contain a 9,9'-spirobifluorene derivative in at least one of the radicals R.

The glass transition temperature of the compounds of the formula (1) is preferably $> 100^{\circ}\text{C}$, particularly preferably $> 120^{\circ}\text{C}$, very particularly preferably $> 140^{\circ}\text{C}$. It has been found that the glass transition temperature of compounds in which at least one of the radicals R contains a spirobifluorene derivative is usually in this range.

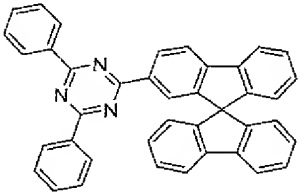
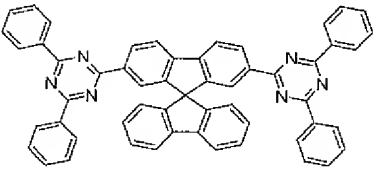
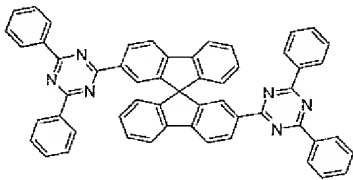
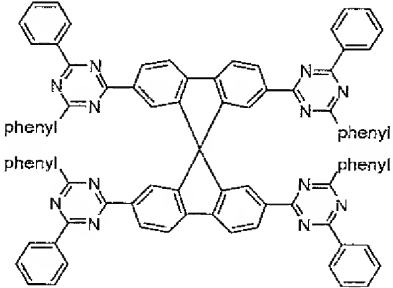
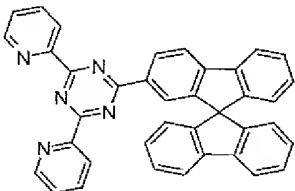
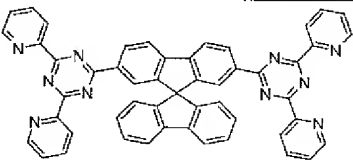
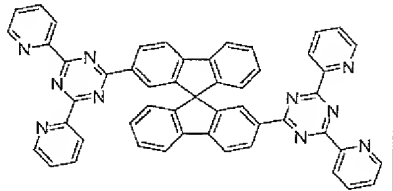
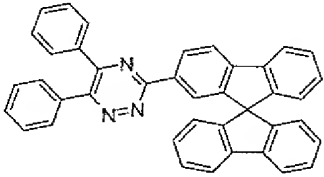
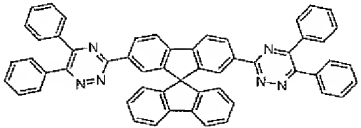
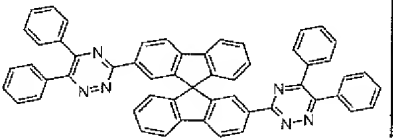
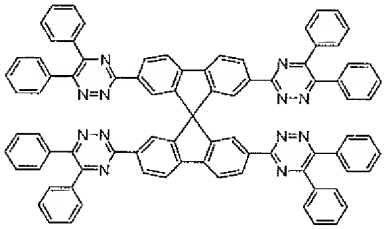
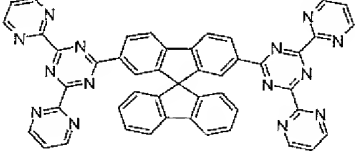
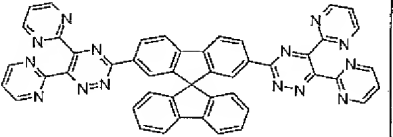
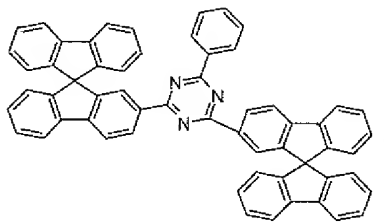
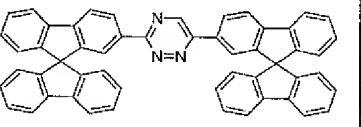
This justifies the preference for these materials.

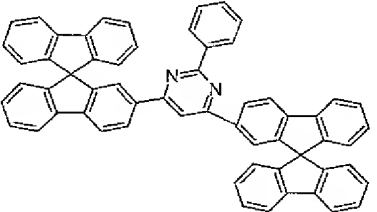
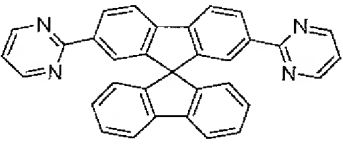
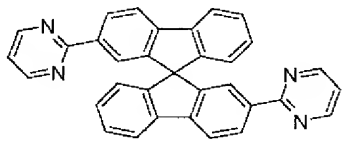
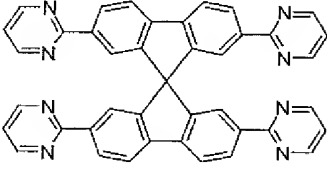
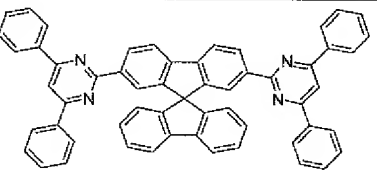
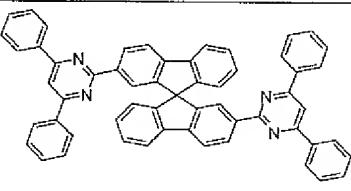
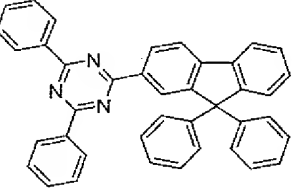
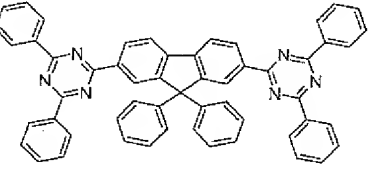
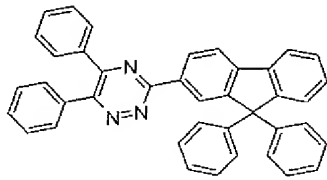
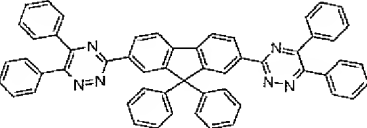
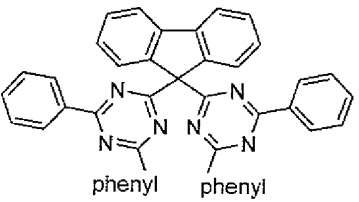
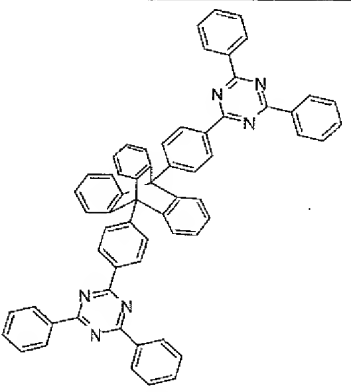
It has been found that the best results (in relation to the efficiency and lifetime) are achieved if the layer thickness of the hole-blocking layer is 1 to 50 nm, preferably 5 to 30 nm.

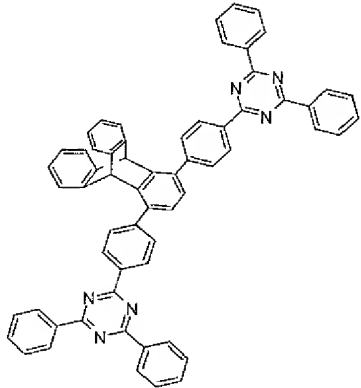
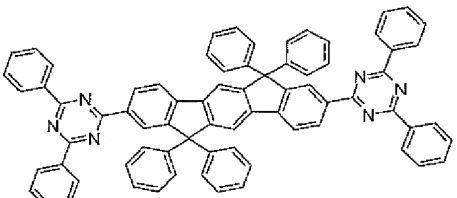
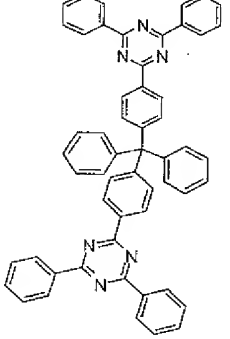
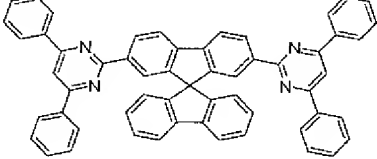
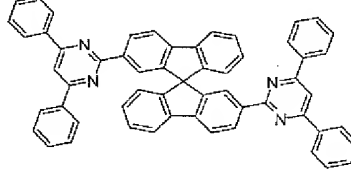
It has furthermore been found that particularly good results are obtained, in particular in relation to the operating voltage and power efficiency, if an electron-transport layer is not incorporated between the hole-blocking layer and the cathode or the electron-injection layer. Preference is thus given to an electroluminescent device according to the invention which does not comprise an electron-transport layer. This is a surprising result since the same device structure with BCP as hole-blocking material without an ETL gives significantly shorter lifetimes.

The present invention is explained in greater detail by the following examples of hole-blocking materials of the formula (1), without wishing to be restricted thereto. Possible substituents on the spirobifluorene unit or the corresponding other units and also the substituents on the triazine are not shown for reasons of clarity. The person skilled in the art will be able to produce further electroluminescent devices

according to the invention comprising similar hole-blocking materials from the description and the examples given without an inventive step.

		
Example 1	Example 2	Example 3
		
Example 4	Example 5	Example 6
		
Example 7	Example 8	Example 9
		
Example 10	Example 11	Example 12
		
Example 13	Example 14	Example 15

		
Example 16	Example 17	Example 18
		
Example 19	Example 20	Example 21
		
Example 22	Example 23	Example 24
		
Example 25	Example 26	Example 27

		
Example 28	Example 29	
		
Example 30	Example 31	Example 32

The matrix for the phosphorescent emitter is preferably selected from the classes of the carbazoles, for example in accordance with WO 00/057676, EP 01/202358 and WO 02/074015, the ketones and imines, for example in accordance with DE 10317556.3, the phosphine oxides, phosphine sulfides, phosphine selenides, the phosphazenes, the sulfones, the sulfoxides, for example in accordance with DE 10330761.3, the silanes, the polypodal metal complexes, for example in accordance with DE 10310887.4, or the oligophenylenes based on spirobifluorenes, for example in accordance with EP 676461 and WO 99/40051; particular preference is given to ketones, phosphine oxides, sulfoxides and oligophenylenes based on spirobifluorenes.

The phosphorescent emitter is preferably a compound which contains at least one element having an atomic number of greater than 36 and less than 84.

The phosphorescent emitter particularly preferably contains at least one element having an atomic number of greater than 56 and less than 80, very particularly preferably molybdenum, tungsten, rhenium, ruthenium, osmium, rhodium, iridium, palladium, platinum, silver, gold or europium, for example in accordance with WO 98/01011, US 02/0034656, US 03/0022019, WO 00/70655, WO 01/41512, WO

02/02714, WO 02/15645, EP 1191613, EP 1191612, EP 1191614, WO 03/040257 and DE 10215010.9.

5 One or more layers in the organic electroluminescent device are preferably coated by a sublimation process, in which the low-molecular-weight materials are vapour-deposited in vacuum sublimation units at a pressure below 10^{-5} mbar, preferably below 10^{-6} mbar, particularly preferably below 10^{-7} mbar.

10 One or more layers in the organic electroluminescent device are likewise preferably coated by the OVPD (organic vapour phase deposition) process or with the aid of carrier-gas sublimation, in which the low-molecular-weight materials are applied at a pressure between 10^{-5} mbar and 1 bar.

15 One or more layers in the organic electroluminescent device are likewise preferably coated by a printing process, such as, for example, flexographic printing or offset printing, but particularly preferably LITI (light induced thermal imaging, thermal transfer printing) or ink-jet printing.

20 The emitting devices described above have the following surprising advantages over the prior art:

1. The efficiency of corresponding devices is higher compared with systems in accordance with the prior art which comprise BAQ as HBL.
2. The lifetime of corresponding devices is longer compared with systems comprising BCP as HBL. Devices are thereby obtained whose lifetime and efficiency are comparable with the best values in accordance with the prior art and in which not only one of the two properties gives good results, as is the case with BAQ or BCP.
3. The operating voltages are lower in devices according to the invention than in devices in accordance with the prior art.
- 30 4. The layer structure can be simplified since there is no need to use an electron-transport layer. This is a surprising result since the same device structure with BCP instead of triazine without an electron-transport layer gives significantly worse lifetimes and efficiencies.
- 35 5. If an electron-transport layer is not used, a further advantage arises: the operating voltages here are significantly lower; the power efficiency consequently increases considerably. This is a surprising result since the same device structure with BAQ instead of triazine results in an operating voltage which is hardly reduced at all.

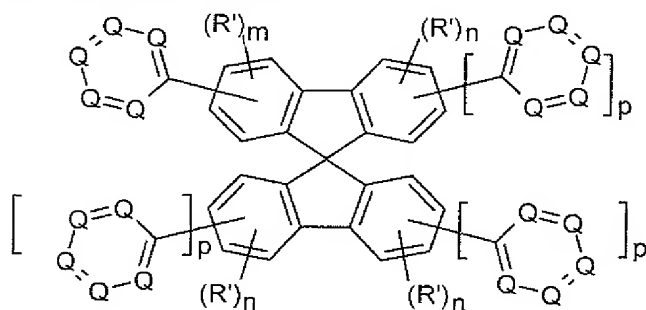
6. The production complexity is likewise less without use of an electron-transport layer. This is a considerable technological advantage in the production process since a separate segment of the vapour-deposition unit is required for each organic layer in the conventional production process.

Details on the statements made here are given in the examples described below.

The present application text and the following examples are directed to organic light-emitting diodes and the corresponding displays. In spite of this restriction of the description, it is possible for the person skilled in the art, without further inventive step, also to use the corresponding design according to the invention for other, related devices, for example for organic solar cells (O-SCs), organic transistors, organic integrated circuits or also organic laser diodes (O-lasers), to mention but a few further applications. The present application therefore also relates to these.

Spirobifluorenes which are substituted by triazines are novel and are thus likewise a subject-matter of the present invention.

The invention thus furthermore relates to compounds of the formula (2) comprising at least one spirobifluorene unit, characterised in that at least one triazine unit is bonded to the spirobifluorene



formula (2)

where R and R¹ have the same meaning as defined above under formula (1), and the further symbols and indices have the following meaning:

- Q is on each occurrence, identically or differently, N or CR, with the proviso that three Q stand for nitrogen and two Q stand for CR;
- R' is on each occurrence, identically or differently, R or F, Cl, Br, I, B(R¹)₂ or B(OR¹)₂;
- m is on each occurrence, identically or differently, 0, 1, 2 or 3;

- n is on each occurrence, identically or differently, 0, 1, 2, 3 or 4, with the proviso that n must not be 4 if p = 1;
- p is on each occurrence, identically or differently, 0 or 1.

- 5 The triazine unit can in accordance with the invention be 1,2,3-, 1,2,4- or 1,3,5-triazine. Various triazine derivatives may also be present in a single compound. All the triazines present in a single compound are preferably the same triazine derivative. Particular preference is given to 1,3,5-triazine or 1,2,4-triazine.
- 10 The triazine unit is preferably linked to the spirobifluorene in position 2 (or 2', 7 or 7'), i.e. in the *para*-position to the phenyl-phenyl link of the spirobifluorene.

In preferred structures of the formula (2), the following applies to the symbols and indices:

- 15 R is on each occurrence, identically or differently, a straight-chain, branched or cyclic alkyl group having 1 to 10 C atoms, in which one or more non-adjacent CH₂ groups may be replaced by -R¹C=CR¹-, -C≡C-, Si(R¹)₂, Ge(R¹)₂, Sn(R¹)₂, -O-, -S- or -NR¹-, or an aromatic or heteroaromatic system having 1 to 30 aromatic C atoms, which may be substituted by one or more non-aromatic radicals
- 20 R, where a plurality of substituents R, both on the same ring and also on different rings, may together in turn form a further mono- or polycyclic, aliphatic or aromatic ring system;
- m is on each occurrence, identically or differently, 0 or 1;
- n is on each occurrence, identically or differently, 0 or 1;
- 25 the further symbols and indices are as defined above under formula (1) and (2).

In particularly preferred structures of the formula (2), the following applies to the symbols and indices:

- 30 R is on each occurrence, identically or differently, an aromatic or heteroaromatic system having 1 to 10 aromatic C atoms, which may be substituted by one or more non-aromatic radicals R, as defined above, where a plurality of substituents R, both on the same ring and also on different rings, may together in turn form a further mono- or polycyclic, aliphatic or aromatic ring system;
- 35 R' is on each occurrence, identically or differently, R, a straight-chain, branched or cyclic alkyl group having 1 to 10 C atoms, in which one or more non-adjacent CH₂ groups may be replaced by -R¹C=CR¹-, -C≡C-, Si(R¹)₂, Ge(R¹)₂, Sn(R¹)₂, -O-, -S- or -NR¹-, or Br, I or B(OR¹)₂;
- m is equal to 0;
- n is on each occurrence, identically or differently, 0 or 1;

the further symbols and indices are as defined above under formula (1) and (2).

Preference is furthermore given to compounds of the formula (2) in which two triazine units are present, both bonded to the same fluorene sub-unit of the spiro-bifluorene, preferably in positions 2 and 7.

The compounds of the formula (2) according to the invention described above can also be used, for example, as comonomers for the production of corresponding polymers or also as the core of dendrimers. Particularly suitable for this purpose are compounds of the formula (2) which contain corresponding functionalities which are suitable for the subsequent reaction, such as, for example, halogens, in particular bromine or iodine, or boronic acids or corresponding derivatives. Thus, these compounds can be copolymerised, inter alia, into soluble polyfluorenes (for example in accordance with EP-A-842208 or WO 00/22026), polyspirobifluorenes (for example in accordance with EP-A- 707020 or EP-A-894107) or polyindenofluorenes (for example in accordance with WO 04/041901 or EP 03014042.0) or polydihydrophenanthrenes (for example in accordance with DE 10337346.2). These polymers or dendrimers can be used as hole-blocking material in organic electroluminescent devices.

The materials of the formula (2) may furthermore also be functionalised further by the reaction types indicated above, for example, and thus converted into extended hole-blocking materials of the formula (2). An example which may be mentioned here is SUZUKI functionalisation using arylboronic acids or HARTWIG-BUCHWALD functionalisation using amines.

The present invention furthermore relates to the use of compounds of the formula (2) or polymers or dendrimers which comprise these compounds, in electronic devices. The invention likewise relates to electronic devices, such as, for example, organic light-emitting diodes, organic solar cells, organic transistors, organic integrated circuits or organic laser diodes, which comprise at least one compound of the formula (2) or a corresponding polymer or dendrimer.

The OLEDs are produced by a general process which has been adapted in individual cases to the respective circumstances (for example layer-thickness variation in order to optimise the efficiency or colour). The hole-blocking layer used for the production of the devices according to the invention was a compound of the formula (1), and the electron-transport layer is optionally omitted. Electroluminescent devices

according to the invention can be produced as described, for example, in DE10330761.3.

Examples:

The following syntheses were carried out, unless indicated otherwise, under a protective-gas atmosphere in dried solvents. The starting materials were purchased from ALDRICH (potassium fluoride (spray-dried), tri-*tert*-butylphosphine, palladium(II) acetate). 3-Chloro-5,6-diphenyl-1,2,4-triazine was purchased from SYNCHEM OHG. 2',7'-di-*tert*-butylspiro-9,9'-bifluorene-2,7-bisboronic acid glycol ester was prepared as described in WO 02/077060, and 2-chloro-4,6-diphenyl-1,3,5-triazine was prepared as described in US 5438138. Spiro-9,9'-bifluorene-2,7-bis(boronic acid glycol ester) was prepared analogously to WO 02/077060.

Example 1: Synthesis of 2,7-bis(4,6-diphenyl-1,3,5-triazin-2-yl)-2',7'-di-*tert*-butylspiro-9,9'-bifluorene (TR11)

To a suspension of 28.4 g (50.0 mmol) of glycol 2',7'-di-*tert*-butylspiro-9,9'-bifluorene-2,7-bisboronate, 29.5 g (110.0 mmol) of 2-chloro-4,6-diphenyl-1,3,5-triazine and 44.6 g (210.0 mmol) of tripotassium phosphate were suspended in 500 ml of toluene, 500 ml of dioxane and 500 ml of water. 913 mg (3.0 mmol) of tri-*o*-tolylphosphine and then 112 mg (0.5 mmol) of palladium(II) acetate were added to this suspension, and the reaction mixture was refluxed for 16 h. After cooling, the organic phase was separated off, filtered through silica gel, washed three times with 200 ml of water and subsequently evaporated to dryness. The residue was recrystallised from toluene and from dichloromethane/isopropanol and finally sublimed in a high vacuum ($p = 5 \times 10^{-5}$ mbar, $T = 385^\circ\text{C}$). The yield was 39.9 g (44.8 mmol), corresponding to 89.5% of theory.

$^1\text{H-NMR}$ (CDCl_3): [ppm] = 8.89 (m, 2H), 8.65 (m, 8H), 8.14 (m, 2H), 8.06 (m, 2H), 7.86 (m, 2H), 7.61-7.50 (m, 12H), 7.47 (m, 2H), 6.79 (m, 2H), 1.16 (s, 18 H).

Example 2: Synthesis of 2,7-bis(4,6-diphenyl-1,3,5-triazin-2-yl)spiro-9,9'-bifluorene (TR12)

Procedure analogous to Example 1, with the 2',7'-di-*tert*-butylspiro-9,9'-bifluorene-2,7-bis(boronic acid glycol ester) being replaced by 22.8 g (50 mmol) of spiro-9,9'-bifluorene-2,7-bis(boronic acid glycol ester). The yield was 32.3 g (41.5 mmol), corresponding to 82.9% of theory.

$^1\text{H-NMR}$ (CDCl_3): [ppm] = 8.90 (m, 2H), 8.64 (m, 8H), 8.14 (m, 2H), 8.09 (m, 2H), 8.01 (m, 2H), 7.61-7.49 (m, 12H), 7.45 (m, 2H), 7.15 (m, 2), 6.86 (m, 2H).

Example 3: Synthesis of 2,7-bis(5,6-diphenyl-1,2,4-triazin-3-yl)-2',7'-di-tert-butylspiro-9,9'-bifluorene (TRI3)

Procedure analogous to Example 1, with the 2-chloro-4,6-diphenyl-1,3,5-triazine being replaced by 3-chloro-5,6-diphenyl-1,2,4-triazine. The yield was 41.0 g (46.0 mmol), corresponding to 92.0% of theory.

¹H-NMR (CDCl₃): [ppm] = 8.74 (m, 2H), 8.12 (m, 4H), 7.75 (m, 2H), 7.59 (m, 4H), 7.53 (m, 4H), 7.45-7.30 (m, 14H), 6.76 (m, 2H) 1.14 (s, 18 H).

Example 4: Device structure

The following examples show the results for various OLEDs, both with hole-blocking materials of the formula (1) and also with BCP and BAQ as comparative materials. The basic structure, the materials and layer thicknesses used (apart from the HBLs) were identical for better comparability. Phosphorescent OLEDs having the following structure were produced by the above-mentioned general process:

PEDOT (HIL)	60 nm (spin-coated from water; purchased as Baytron P from H.C. Starck; poly-(3,4-ethylenedioxy-2,5-thiophene))
NaphDATA (HTL)	20 nm (vapour-deposited; purchased from SynTec; 4,4',4''-tris-(N-1-naphthyl-N-phenylamino)triphenylamine)
S-TAD (HTL)	20 nm (vapour-deposited; prepared as described in WO 99/12888; 2,2',7,7'-tetrakis(diphenylamino)spirobifluorene)
(EML)	30 nm (vapour-deposited); 10% of IrPPy in bis(9,9'-spirobifluorene-2-yl) ketone as matrix material
(HBL)	materials and layer thicknesses see examples in Table 1
AlQ ₃ (ETL)	not present in all devices (see Table 1); if present: vapour-deposited (purchased from SynTec; tris(8-hydroxyquinolato)aluminum(III))
Ba/Al (cathode)	3 nm Ba, 150 nm Al on top.

These still unoptimised OLEDs were characterised by standard methods; for this purpose, the electroluminescence spectra, the efficiency (measured in cd/A), the power efficiency (measured in lm/W) as a function of the brightness and the lifetime were determined. The lifetime is defined as the time after which the initial brightness of the OLED has dropped to half at a constant current density of 10 mA/cm².

Table 1 shows the results for the OLEDs according to the invention and some comparative examples (with BCP and BAQ) (Examples 5 to 8). The table only shows the hole-blocking layer (composition and layer thickness). The other layers correspond

to the above-mentioned structure. In Example 5, TRI1 is used together with an ETL, in Example 6 without an ETL. In Example 7, TRI2 is used together with an ETL, in Example 8 without an ETL.

- 5 The abbreviations used above and in Table 1 correspond to the following compounds:

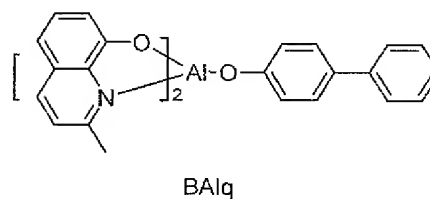
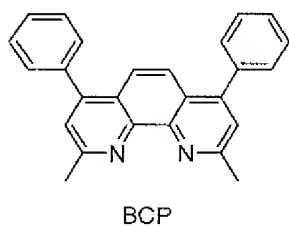
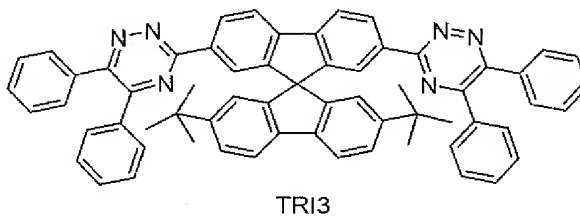
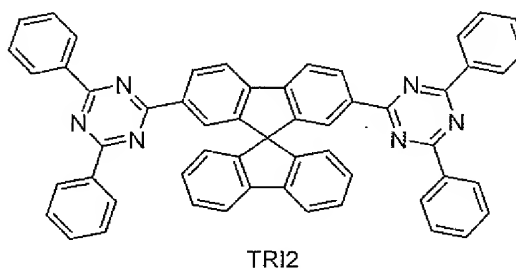
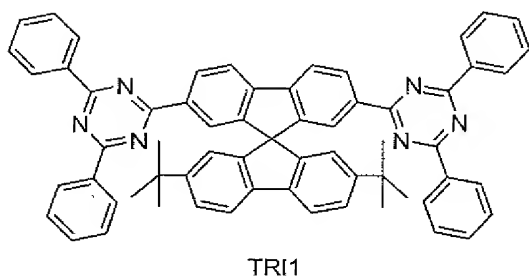
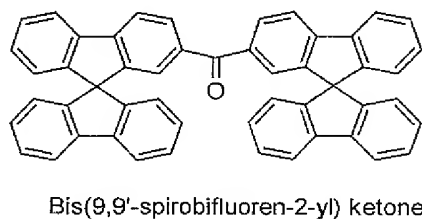
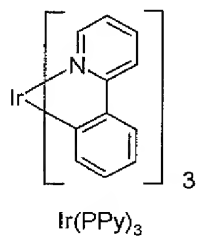


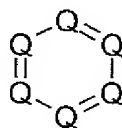
Table 1:

Example	HBL	ETL	Max. efficiency (cd/A)	Voltage (V) at 100 cd/m ²	Power efficiency (lm/W) at max. efficiency	CIE (x, y)	Lifetime (h) at 10mA/cm ²
Example 5a	TRI1 (10 nm)	AlQ ₃ (20 nm)	33.5	4.3	22.1	0.39 / 0.57	780
Example 5b (comp.)	BAlq (10 nm)	AlQ ₃ (20 nm)	25.2	5.7	14.8	0.39 / 0.57	510
Example 5c (comp.)	BCP (10 nm)	AlQ ₃ (20 nm)	32.6	4.8	18.2	0.39 / 0.57	360
Example 6a	TRI1 (20 nm)	—	34.2	2.7	41.4	0.38 / 0.58	310
Example 6b (comp.)	BAlq (20 nm)	—	24.8	5.2	14.7	0.39 / 0.58	240
Example 6c (comp.)	BCP (20 nm)	—	16.7	4.8	8.7	0.32/0.62	80

Example 7a	TRI2 (10 nm)	AlQ ₃ (20 nm)	30.9	4.0	19.2	0.39 / 0.58	770
Example 7b (comp.)	see Examples 5b and 5c						
Example 8a	TRI2 (20 nm)	---	32.9	2.9	33.8	0.38 / 0.58	320
Example 8b (comp.)	see Examples 6b and 6c						

In summary, it can be stated that phosphorescent OLEDs which comprise hole-blocking materials of the formula (1) or of the formula (2) have high efficiencies at the same time as long lifetimes and low operating voltages, as can easily be seen from the examples in Table 1. In particular without using an electron-transport layer, very low operating voltages and very high power efficiencies are obtained.

1. Organic electroluminescent device comprising an anode, a cathode and an emission layer, consisting of at least one matrix material which is doped with at least one phosphorescent emitter, characterised in that a hole-blocking layer which comprises a compound of the formula (1)



(formula 1)

where the following applies to the symbols and indices used:

- Q is on each occurrence, identically or differently, N or CR, with the proviso that at least two and a maximum of four Q stand for nitrogen;
- R is on each occurrence, identically or differently, H, NO₂, CN, N(R¹)₂, a straight-chain, branched or cyclic alkyl or alkoxy group having 1 to 40 C atoms, in which one or more non-adjacent CH₂ groups may be replaced by -R¹C=CR¹-, -C≡C-, Si(R¹)₂, Ge(R¹)₂, Sn(R¹)₂, -O-, -S- or -NR¹- and in which one or more H atoms may be replaced by F, -NR¹- or an aromatic group R¹, or an aromatic or heteroaromatic system or an aryloxy or heteroaryloxy group, each having 1 to 40 aromatic C atoms, in which one or more H atoms may be replaced by F, Cl, Br or I or which may be substituted by one or more non-aromatic radicals R, where a plurality of substituents R may form a further mono- or polycyclic, aliphatic or aromatic ring system, or an aromatic or heteroaromatic system bonded via a divalent group -Z- or an aryloxy or heteroaryloxy group, each having 1 to 40 aromatic C atoms, in which one or more H atoms may be replaced by F, Cl, Br or I or which may be substituted by one or more non-aromatic radicals R, where a plurality of substituents R may form a further mono- or polycyclic, aliphatic or aromatic ring system, or;
- R¹ is on each occurrence, identically or differently, H or an aliphatic, aromatic or heteroaromatic hydrocarbon radical having 1 to 20 C atoms, in which a plurality of substituents R¹ or R¹ with R may also form a further mono- or polycyclic, aliphatic or aromatic ring system, and
- Z is a straight-chain, branched or cyclic, preferably conjugated radical having 1 to 40 C atoms, which is preferably in conjugation with the two other substituents, where the number of atoms in Z which link the group of the formula (1) and the aromatic radical is preferably an even number, where one or more non-adjacent

cent C atoms may be replaced by -O-, -S- or -NR¹- or one or more C atoms may be substituted by a radical R¹ or halogen, is incorporated between the emission layer and the cathode.

2. Organic electroluminescent device according to Claim 1, characterised in that a hole-injection layer and/or a hole-transport layer and/or an electron-injection layer and/or an electron-transport layer is present.
3. Organic electroluminescent device according to Claim 1 and/or 2, characterised in that the hole-blocking layer comprises at least 50% of compounds of the formula (1).
4. Organic electroluminescent device according to Claim 3, characterised in that the hole-blocking layer consists only of compounds of the formula (1).
5. Organic electroluminescent device according to one or more of Claims 1 to 4, characterised in that the structures of the formula (1) are selected from the groups of the pyridazines, pyrimidines, pyrazines, 1,2,3-, 1,2,4- or 1,3,5-triazines.
6. Organic electroluminescent device according to Claim 5, characterised in that the structures of the formula (1) are selected from the groups of the 1,2,4-triazines or 1,3,5-triazines.
7. Organic electroluminescent device according to one or more of Claims 1 to 6, characterised in that the hole-blocking material comprises more than one unit of the formula (1).
8. Organic electroluminescent device according to one or more of Claims 1 to 7, characterised in that the molecules of the hole-blocking material have a non-planar structure.
9. Organic electroluminescent device according to Claim 8, characterised in that at least one substituent R in the hole-blocking material contains at least one sp³-hybridised carbon atom.
10. Organic electroluminescent device according to Claim 9, characterised in that the sp³-hybridised carbon atom is a quaternary carbon atom.

11. Organic electroluminescent device according to Claim 10, characterised in that in compounds of the formula (1), a 9,9'-spirobifluorene derivative, a 9,9-disubstituted fluorene derivative, a 6,6- and/or 12,12-di- or tetrasubstituted indenofluorene derivative, a tetraarylmethane derivative or a triptycene derivative is present in at least one of the radicals R.

12. Organic electroluminescent device according to Claim 11, characterised in that in compounds of the formula (1), a 9,9'-spirobifluorene derivative is present in at least one of the radicals R.

13. Organic electroluminescent device according to one or more of Claims 1 to 12, characterised in that the glass transition temperature of the compounds of the formula (1) is $> 100^{\circ}\text{C}$.

14. Organic electroluminescent device according to one or more of Claims 1 to 13, characterised in that the layer thickness of the hole-blocking layer is 1 to 50 nm.

15. Organic electroluminescent device according to one or more of Claims 1 to 14, characterised in that the matrix for the phosphorescent emitter is selected from the classes of the carbazoles, ketones, imines, phosphine oxides, phosphine sulfides, phosphine selenides, phosphazenes, sulfones, sulfoxides, silanes, polypodal metal complexes or oligophenylenes based on spirobifluorenes.

16. Organic electroluminescent device according to one or more of Claims 1 to 15, characterised in that the phosphorescent emitter is a compound which contains at least one element having an atomic number of greater than 36 and less than 84.

17. Organic electroluminescent device according to Claim 16, characterised in that the phosphorescent emitter contains at least one element selected from the elements molybdenum, tungsten, rhenium, ruthenium, osmium, rhodium, iridium, palladium, platinum, silver, gold and europium.

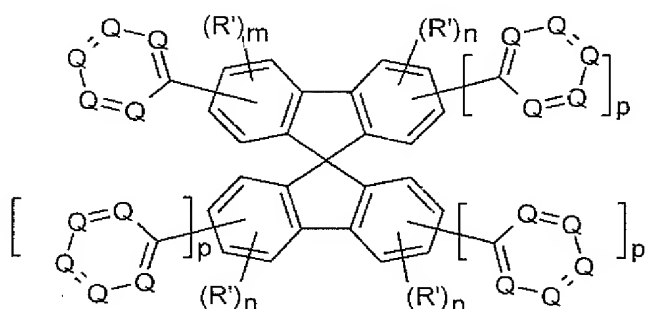
18. Organic electroluminescent device according to one or more of Claims 1 to 17, characterised in that one or more layers are coated by a sublimation process.

19. Organic electroluminescent device according to one or more of Claims 1 to 17, characterised in that one or more layers are coated by the OVPD (organic vapour phase deposition) process or with the aid of carrier-gas sublimation.

20. Organic electroluminescent device according to one or more of Claims 1 to 17, characterised in that one or more layers are coated by a printing process.

21. Use of the design of the electronic devices according to one or more of Claims 1 to 17 for organic transistors, organic integrated circuits, organic solar cells, organic laser diodes or photoreceptors.

22. Compounds of the formula (2) comprising at least one 9,9'-spirobifluorene unit, characterised in that at least one triazine unit is bonded to the 9,9'-spirobifluorene



formula (2)

where R and R¹ have the same meaning as defined in Claim 1, and the further symbols and indices have the following meaning:

Q is on each occurrence, identically or differently, N or CR, with the proviso that three Q stand for nitrogen and two Q stand for CR;

R' is on each occurrence, identically or differently, R or F, Cl, Br, I, B(R¹)₂ or B(OR¹)₂;

m is on each occurrence, identically or differently, 0, 1, 2 or 3;

n is on each occurrence, identically or differently, 0, 1, 2, 3 or 4, with the proviso that n must not be 4 if p = 1;

p is on each occurrence, identically or differently, 0 or 1.

23. Compounds according to Claim 22, characterised in that 1,2,4-triazine or 1,3,5-triazine is involved.

24. Compounds according to Claim 22 and/or 23, characterised in that the following applies to the symbols and indices:

R is on each occurrence, identically or differently, an aromatic or heteroaromatic system having 1 to 10 aromatic C atoms, which may be substituted by

one or more non-aromatic radicals R, where a plurality of substituents R, both on the same ring and also on different rings, may together in turn form a further mono- or polycyclic, aliphatic or aromatic ring system;

R' is on each occurrence, identically or differently, R, a straight-chain, branched or cyclic alkyl group having 1 to 10 C atoms, in which one or more non-adjacent CH₂ groups may be replaced by -R¹C=CR¹-, -C≡C-, Si(R¹)₂, Ge(R¹)₂, Sn(R¹)₂, -O-, -S- or -NR¹-, or Br, I or B(OR¹)₂;

m is on each occurrence equal to 0;

n is on each occurrence, identically or differently, 0 or 1;

the further symbols and indices are as defined above under formula (1) and (2).

25. Compounds according to one or more of Claims 22 to 24, characterised in that two triazine units are present, both bonded to the same fluorene sub-unit of the spirobifluorene.

26. Polymers or dendrimers comprising one or more compounds according to one or more of Claims 22 to 25.

27. Use of compounds, polymers or dendrimers according to one or more of Claims 22 to 26 in electronic devices.

28. Electronic device according to Claim 27, characterised in that organic light-emitting diodes, organic solar cells, organic transistors, organic integrated circuits, organic laser diodes or organic photoreceptors are involved.

Organic electroluminescent element

5 The present invention relates to the improvement of phosphorescent organic electroluminescent devices by using materials of the formula (1), preferably triazines, pyrimidines, pyridazines and pyrazines, in the hole-blocking layer.